

## Analysis of bulk modulus and thermal expansivity for six minerals at high temperatures

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**Abstract** : The data on isothermal bulk modulus and thermal expansivity for six minerals (MgO, Mg<sub>2</sub>SiO<sub>4</sub>, Al<sub>2</sub>O<sub>3</sub>, Grossular Garnet, Pyrope and CaO) at high temperatures are analysed in order to obtain simple empirical relationships. Various thermodynamic formulations reported in the recent literature, have been discussed and evaluated critically. The thermodynamic model due to Xia and Xiao has been found to yield good agreement with experimental data for thermal expansivity as a function of temperature for all the minerals under study.

**Keywords** : Bulk modulus, thermal expansivity, geophysical minerals

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### 1. Introduction

One of the most widely used thermodynamic approximations [1–4] for studying the high temperature-high pressure behaviour of solids is that the product of volume thermal expansion coefficient, *i.e.* the thermal expansivity  $\alpha$  and the isothermal bulk modulus  $B$  remains constant. Thus, we can write

$$\alpha B = K, \quad (1)$$

where the product  $K$  has been assumed to remain constant under the variation of pressure or temperature. If this assumption does not hold, then eq. (1) yields the following relationship for the isobaric variation of  $\alpha$ ,  $B$  and  $K$  with the change in volume under the effect of temperature,

$$\frac{V}{\alpha} \left( \frac{d\alpha}{dV} \right)_p + \frac{V}{B} \left( \frac{dB}{dV} \right)_p = \frac{V}{K} \left( \frac{dK}{dV} \right)_p. \quad (2)$$

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The data reported by Anderson *et al* [5] for six minerals at high temperatures, are used in the present study to assess the validity of basic assumptions regarding the variations of  $\alpha$ ,  $B$  and  $K$  with temperature. In particular, we study the variation of  $\alpha$  and volume with temperature using the thermodynamic model due to Xia and Xiao [6]. The method of analysis is presented in Section 2. Results are discussed and compared with experimental data in Section 3.

## 2. Method of analysis

Taking the high temperature data from Anderson *et al* [5], we made an attempt to plot  $\alpha$ ,  $B$  and  $K$ , each as a function of  $V/V_0$ , where  $V_0$  is the volume  $V$  at 300 K. Values of  $V/V_0$  corresponding to different temperatures were estimated from the data on density [5]. Systematic linear relationships are obtained only for  $\ln B$  versus  $\ln V/V_0$  for all the six minerals [Figures 1(a–f)]. Plots for  $\ln \alpha$  or  $\ln K$  versus  $\ln V/V_0$  are found to be unsystematic and non-linear. Thus,  $\alpha$  or  $K$  depends on the change in volume in a complicated manner. On the other hand, the slopes of the linear plots in Figures 1(a–f) yield values of the Anderson-Gruneisen parameter  $\delta_T$  which is defined as [5,7]

$$\delta_T = -\frac{1}{\alpha B} \left( \frac{dB}{dT} \right)_p \quad (3)$$

Using  $\alpha = \frac{1}{V} \left( \frac{dV}{dT} \right)_p$  in eq. (3), we get

$$\delta_T = - \left( \frac{d \ln B}{d \ln V} \right)_p \quad (4)$$

Thus,  $\delta_T$  represents the slope of the plots of  $\ln B$  versus  $\ln (V/V_0)$ . Values of  $\delta_T$  determined from the plots given in Figures 1(a–f) are reported in Table 1.

If the product  $K = \alpha B$  is assumed to remain constant with the variation in temperature then eq. (2) yields

$$\frac{V}{\alpha} \left( \frac{d\alpha}{dV} \right)_p = -\frac{V}{B} \left( \frac{dB}{dV} \right)_p \quad (5)$$

which can also be written in the following form [7]

$$\frac{1}{\alpha^2} \left( \frac{d\alpha}{dT} \right)_p = \delta_T \quad (6)$$

Anderson *et al* [7] have used eq. (6) to obtain the relationship given below

$$\frac{\alpha}{\alpha_0} = \left[ 1 - \alpha_0 \delta_T (T - T_0) \right]^{-1} \quad (7)$$

Eq. (7) has been derived by the integration of (6) taking  $\delta_T$  as constant. Under the same thermodynamic assumptions, the following relationships can also be obtained from eqs. (5) and (7)

$$\frac{\alpha}{\alpha_0} = \left( \frac{V}{V_0} \right)^{\delta_T} \tag{8}$$

and 
$$\frac{V}{V_0} = [1 - \alpha_0 \delta_T (T - T_0)]^{-1/\delta_T} . \tag{9}$$

Eq. (7) is equivalent to (8) in view of (9). As pointed out by Anderson *et al* [7], the assumptions implied in the derivation of the relationships (5 to 9) are valid only in the high temperature region above the Debye temperature.

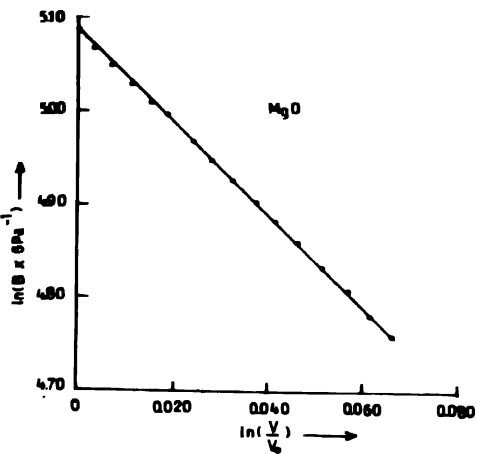


Figure 1(a). Plots of  $\ln B$  versus  $\ln (V/V_0)$  at high temperatures

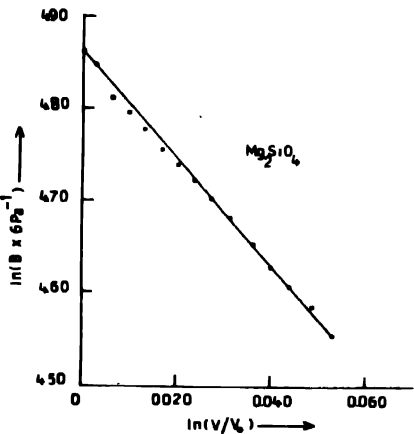


Figure 1(b). Same as in Figure 1(a).

Recently Xia and Xiao [6] have developed a thermodynamic model for investigating  $\alpha$  of periclase (MgO) as a function of temperature. The pressure derivative of heat capacity  $C_p$  can be expressed by the following thermodynamic identity

$$\left(\frac{dC_p}{dP}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_P. \tag{10}$$

Using the definition of thermal expansivity  $\alpha$ , we can rewrite eq. (10) as follows

$$\left(\frac{dC_p}{dP}\right)_T = -T\frac{d}{dT}(\alpha V)_P. \tag{11}$$

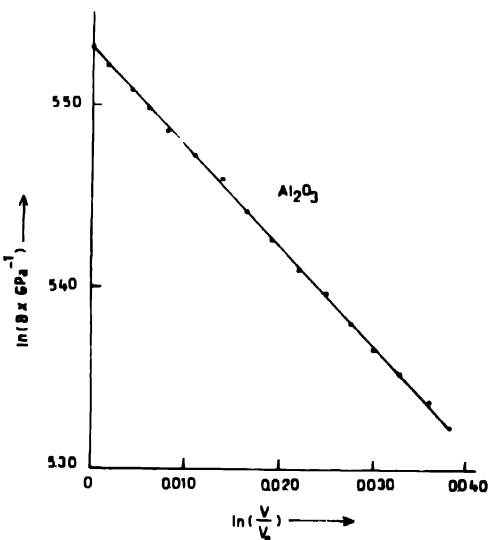


Figure 1(c). Same as in Figure 1(a)

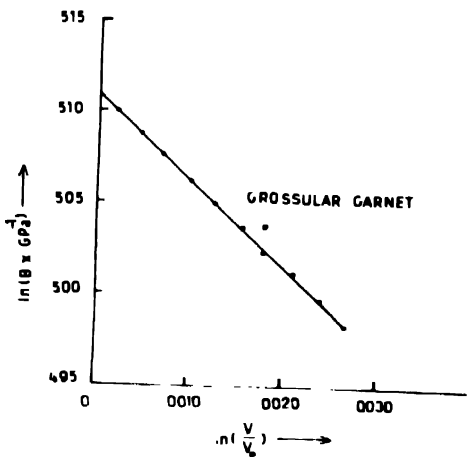


Figure 1(d). Same as in Figure 1(a).

It has been found that in the range of elastic Debye temperature, the best fit to the experimental data is represented by the following relationship [6]

$$C_p = C_p^0 - \eta P \quad (12)$$

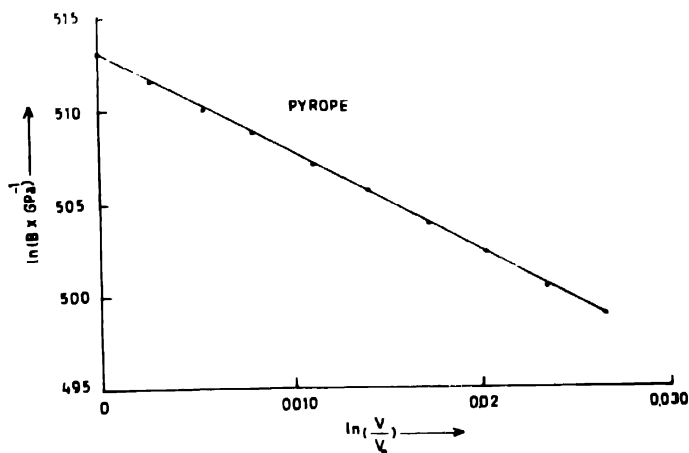


Figure 1(e). Same as in Figure 1(a)

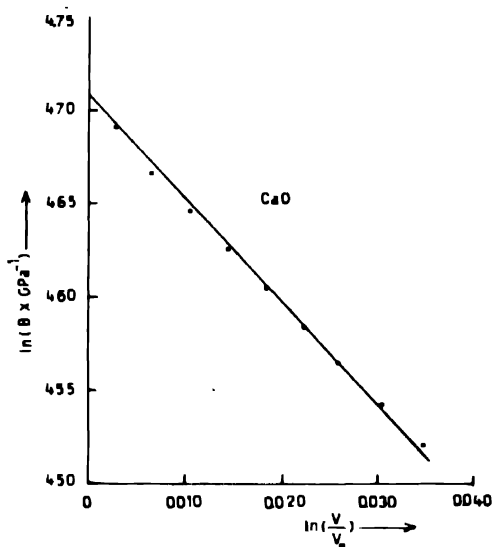


Figure 1(f). Same as in Figure 1(a)

where  $C_p^0$  is the heat capacity at zero pressure and  $\eta$  is a positive constant independent of pressure and temperature. Eqs. (11) and (12) yield

$$\frac{d}{dT}(\alpha V) = \frac{\eta}{T} \quad (13)$$

Attempts have also been made [1,8] to develop models for predicting  $\alpha$  as a function of temperature by incorporating the variation of  $\delta_T$  with volume and temperature.

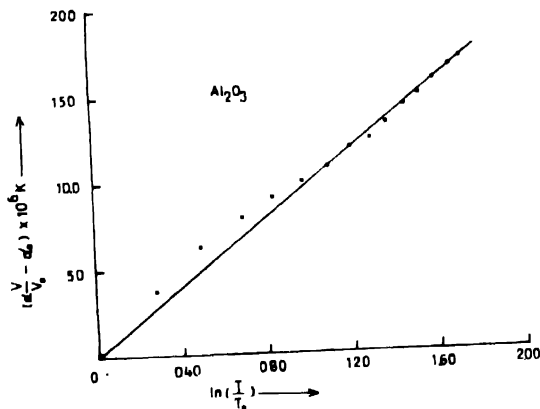


Figure 2(c). Same as in Figure 2(a)

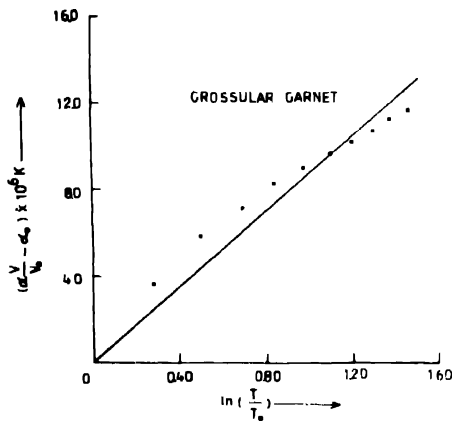


Figure 2(d). Same as in Figure 2(a).

Thus, Tallon [1] has considered that  $\delta_T$  varies as  $V/V_0$  and obtained the following expression for thermal expansivity

$$\alpha = \alpha_0 \exp \left[ \delta_T^0 \left( \frac{V}{V_0} - 1 \right) \right], \quad (18)$$

where  $\delta_T^0$  is the value of  $\delta_T$  at initial temperature. Chopelas and Boehler [9] have shown that  $(\delta_T + 1)$  varies as  $V/V_0$  under the effect of pressure. Considering the similar variation under the effect of temperature also, Kumar and Bedi [8] obtained the following expression

$$\alpha = \alpha_0 \left( \frac{V}{V_0} \right)^{-1} \exp \left[ (\delta_T^0 + 1) \left( \frac{V}{V_0} - 1 \right) \right]. \quad (19)$$

Eqs (18) and (19) have been derived incorporating the variation of  $\delta_T$  in the following formula

$$\frac{V}{\alpha} \left( \frac{d\alpha}{dV} \right) = \delta_T. \quad (20)$$

We have used eqs. (18) and (19) to calculate  $\alpha$  as a function of  $V/V_0$  and temperature. It is found that both the equations yield almost identical results which are smaller than the experimental data by about 15 to 40 per cent.

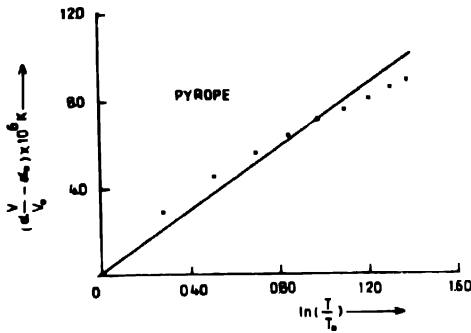


Figure 2(e). Same as in Figure 2(a).

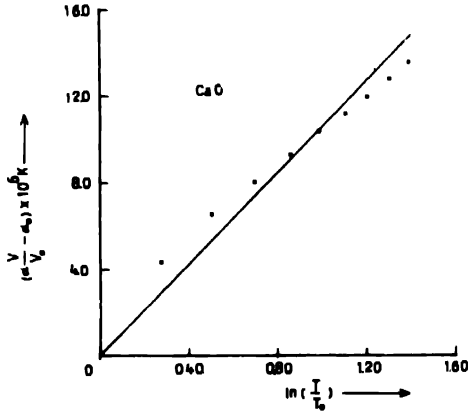


Figure 2(f). Same as in Figure 2(a).

Kumar and Bedi [8] have used the following relationship also for the temperature dependence of  $\delta_T$

$$\delta_T = \delta_T^0 \left( \frac{T}{T_0} \right)^x, \quad (21)$$

where  $x$  is an empirically fitted parameter. Using eqs. (6) and (21) they obtained

$$\frac{\alpha}{\alpha_0} = \left[ 1 - \frac{\alpha_0 \delta_T^0}{T_0^x (x+1)} (T^{x+1} - T_0^{x+1}) \right]^{-1}. \quad (22)$$

Table 2. Values of  $V/V_0$  and thermal expansivity  $\alpha$  ( $10^{-6} \text{ K}^{-1}$ ) for six minerals (a) Values calculated from eqs (15) and (16) due to Xia and Xiao [6], and (b) experimental values [5]

Temperature (K)	MgO				Mg <sub>2</sub> SiO <sub>4</sub>			
	$V/V_0$		$\alpha$		$V/V_0$		$\alpha$	
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	2	3	4	5	6	7	8	9
300	-	-	31.2	31.2	-	-	27.2	27.2
400	1.0033	1.0033	34.9	35.7	1.0029	1.0028	30.4	30.3
500	1.0070	1.0073	37.7	38.4	1.0061	1.0059	32.9	32.2
600	1.0109	1.0112	40.0	40.2	1.0095	1.0094	34.8	33.6
700	1.0150	1.0153	41.8	41.4	1.0131	1.0129	36.5	34.8
800	1.0194	1.0196	43.4	42.6	1.0169	1.0164	37.8	35.9
900	1.0239	1.0240	44.7	43.8	1.0208	1.0199	39.0	37.0
1000	1.0285	1.0284	45.9	44.7	1.0248	1.0238	40.1	38.1
1100	1.0333	1.0331	46.9	45.6	1.0290	1.0277	41.0	39.2
1200	1.0382	1.0379	47.8	46.5	1.0333	1.0320	41.8	40.5
1300	1.0432	1.0427	48.6	47.1	1.0376	1.0363	42.5	41.6
1400	1.0484	1.0476	49.3	48.0	1.0421	1.0407	43.1	42.7
1500	1.0536	1.0528	49.9	48.9	1.0466	1.0451	43.7	43.9
1600	1.0589	1.0581	50.5	49.8	1.0512	1.0498	44.2	45.0
1700	1.0643	1.0635	51.0	50.4	1.0559	1.0547	44.7	46.2
1800	1.0697	1.0688	51.5	51.3	-	-	-	-



Table 2. (Continued)

Temperature (K)	Al <sub>2</sub> O <sub>3</sub>						Grossular Garnet					
	V/V <sub>0</sub>			$\alpha$			V/V <sub>0</sub>			$\alpha$		
	(a)	(b)	3	(a)	(b)	4	(a)	(b)	6	(a)	(b)	7
	2				5					8		9
1												
300	-	-	-	16.2	16.2	16.2	-	-	-	19.2	19.2	19.2
400	1.0018	1.0018	1.0018	18.7	19.9	18.7	1.0021	1.0022	1.0021	21.6	22.8	22.8
500	1.0038	1.0040	1.0040	21.1	22.3	21.1	1.0043	1.0044	1.0043	23.5	24.9	24.9
600	1.0060	1.0063	1.0063	22.9	24.0	22.9	1.0068	1.0073	1.0068	25.0	26.1	26.1
700	1.0080	1.0083	1.0083	24.2	25.1	24.2	1.0093	1.0098	1.0093	26.2	27.1	27.1
800	1.0109	1.0114	1.0114	25.5	25.9	25.5	1.0121	1.0126	1.0121	27.3	27.8	27.8
900	1.0135	1.0140	1.0140	26.6	26.6	26.6	1.0149	1.0155	1.0149	28.2	28.3	28.3
1000	1.0163	1.0168	1.0168	27.5	27.3	27.5	1.0178	1.0184	1.0178	29.0	28.8	28.8
1100	1.0191	1.0195	1.0195	28.4	28.0	28.4	1.0208	1.0213	1.0208	29.8	29.2	29.2
1200	1.0221	1.0223	1.0223	29.1	28.8	29.1	1.0238	1.0242	1.0238	30.4	29.7	29.7
1300	1.0251	1.0252	1.0252	29.8	29.6	29.8	1.0270	1.0274	1.0270	31.0	30.0	30.0
1400	1.0282	1.0279	1.0279	30.4	30.3	30.4						
1500	1.0313	1.0308	1.0308	31.0	30.9	31.0						
1600	1.0346	1.0337	1.0337	31.5	31.5	31.5						
1700	1.0379	1.0364	1.0364	32.0	32.0	32.0						
1800	1.0412	1.0394	1.0394	32.4	32.5	32.4						

Table 2. (Cont'd)

Temperature (K)	Pyrope						CaO					
	$V/V_0$		$\alpha$		$1/V_0$		$1/V_0$		$\alpha$			
	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)	(a)	(b)
1	2	3	4	5	6	7	8	9				
300	-	-	23.6	23.6	-	-	30.4	30.4				
400	1.0025	1.0027	25.6	26.4	1.0032	1.0033	33.4	34.7				
500	1.0051	1.0054	27.2	28.0	1.0067	1.0066	35.6	36.7				
600	1.0079	1.0082	28.4	29.0	1.0104	1.0106	37.4	38.1				
700	1.0109	1.0112	29.5	29.7	1.0142	1.0145	38.8	39.2				
800	1.0139	1.0142	30.3	30.3	1.0182	1.0186	40.1	40.1				
900	1.0170	1.0173	31.1	30.7	1.0224	1.0226	41.1	40.8				
1000	1.0202	1.0203	31.8	31.1	1.0266	1.0267	42.0	41.4				
1100	1.0235	1.0238	32.3	31.5	1.0310	1.0311	42.8	42.0				
1200	1.0268	1.0269	32.8	31.8	1.0355	1.0356	43.5	42.6				

When we apply this formula to the minerals for reproducing  $\alpha$  at high temperatures (1200–1800 K), the values of  $x$  are required to remain between 0.4 and 1.4. This would imply from eq. (21) that  $\delta_T$  increases very fast with temperature and becomes 2 to 6 times its value at room temperature. Such a large variation in the value of  $\delta_T$  is not consistent with the studies reported in literature [5–7].

It should be mentioned here that a number of relationships showing linear and non-linear dependences of  $\alpha$  on temperature, have been reviewed and studied by Plymate and Stout [10]. These relationships when applied to minerals [11], yield results which deviate much from the experimental data. The thermodynamic model which has been found to yield close agreement with experimental data is that due to Xia and Xiao [6]. The basic assumption used in this model is given by eq. (12), in which  $\eta$  remains nearly constant at different temperatures. The validity of this assumption has been demonstrated by Xia and Xiao by calculating the thermal expansivity of MgO upto 1800 K in good agreement with experimental data. The minerals under study remain in the solid phase for the temperature range considered here. Their thermoelastic properties in the solid phase for the entire temperature range have been determined experimentally by Anderson *et al* [5]. No phase transition to liquid or gaseous state has been observed in this temperature range [7]. We can therefore, assume the approximate validity of eq. (12) in the same solid phase for the minerals.

It is clear from the Figures 2(a–f) that the relationship given by eq. (16) is satisfied approximately well, within a few per cent, with the experimental data for the minerals under study. To a good approximation we can therefore, take the proportionality constant  $A = \eta/V_0$  to be independent of temperature. Using this assumption, we have derived the relationship (eq. 15) between  $V/V_0$  and temperature. We have calculated the values of thermal expansivity  $\alpha$  and  $V/V_0$  as a function of temperature using eqs. (15) and (16). The results are compared with the experimental data in Table 2. The good agreement between the calculated and experimental values of  $\alpha$  and  $V/V_0$  support the validity of the assumption used. Thus, the thermodynamic model due to Xia and Xiao developed recently for MgO [6,11] is also applicable for other minerals under study and provides a simple method for calculating  $\alpha$  and  $V/V_0$  in agreement with the experimental data (Table 2).

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